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DREV REPORT 4296/83
FILE: 3621C-007
MARCH 1983

CRDV RAPPORT 4296/83
DOSSIER: 3621C-007
MARS 1983

CHARACTERIZATION OF NITROCELLULOSE IN SOLUTION

E. Ahad

Centre de Recherches pour la Défense
Defence Research Establishment
Valcartier, Québec

BUREAU - RECHERCHE ET DEVELOPPEMENT
MINISTERE DE LA DÉFENSE NATIONALE
CANADA

RESEARCH AND DEVELOPMENT BRANCH
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CANADA

NON CLASSIFIÉ

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E. Ahad

CENTRE DE RECHERCHES POUR LA DÉFENSE

DEFENCE RESEARCH ESTABLISHMENT

VALCARTIER

Tel: (418) 844-4271

Québec, Canada

March/mars 1983

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ABSTRACT

One cotton nitrocellulose (NC) and four wood NC samples were characterized at 25°C by viscometry, membrane osmometry, gel permeation chromatography (GPC) and light scattering (LS). In most of the methods investigated, the results varied according to the technique used to clarify the solutions. The Huggins parameter computed from the viscosity measurements was practically constant in tetrahydrofuran (THF) but was higher in acetone and ethyl acetate in the case of cotton and high-grade wood NC (13.4% N). GPC measurements were carried out in THF; a concentration effect was observed and molecular weight averages were extrapolated to zero concentration. The polydispersity of the samples was relatively high. LS measurements were carried out in THF and ethyl acetate at 546 and 436 nm. NC in solution consists of a molecularly dispersed portion and a microgel portion that can be reduced by centrifugation and by lowering the solution concentration. The presence of microgels in the solutions produced distortions in Zimm plots, i.e. a marked curvature in the angular dependence of scattering and a deviation from linearity in the concentration dependence. The slope at high angles yielded the ratio of the Z average mean square radius of gyration to the weight average molecular weight.

RÉSUMÉ

Un échantillon de nitrocellulose (NC) de coton et quatre échantillons de NC de bois ont été caractérisés à 25°C par viscosimétrie, osmométrie à membrane, chromatographie par perméation de gel ("GPC") et diffusion de la lumière (DL). Dans la plupart des méthodes examinées, les résultats variaient selon la technique utilisée pour clarifier les solutions. Le paramètre de Huggins calculé à partir des mesures de viscosité était pratiquement constant dans le tétrahydrofurane (THF), mais était plus élevé dans l'acétone et l'acétate d'éthyle dans le cas du NC de coton et du NC de bois "high grade" (13.4% N). Les mesures de GPC ont été effectuées dans le THF; un effet de concentration a été observé et les masses moléculaires moyennes ont été extrapolées à concentration nulle. La polydispersité des échantillons était relativement élevée. Les mesures de DL ont été effectuées dans le THF et l'acétate d'éthyle à 546 et 436 nm. Le NC en solution se compose d'une portion moléculaire dispersée et d'une portion de microgel qui peut être réduite par centrifugation et en diminuant la concentration de la solution. La présence de microgels dans les solutions produisait des distorsions dans les diagrammes de Zimm, i.e. une courbure prononcée dans la variation angulaire de la diffusion et une déviation de la linéarité pour la variation de la diffusion avec la concentration. La pente aux angles élevés a fourni le rapport entre la moyenne "Z" du carré moyen du rayon de giration et la moyenne pondérale de la masse moléculaire.

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NOMENCLATURE

A_2	second virial coefficient
a	the exponent in the Mark-Houwink relation
c	the concentration (expressed in g/dl in viscosity, g/L in osmometry and g/ml in LS)
(dn/dc)	the specific refractive index increment for the solute-solvent system
f	Cabannes' factor
G	shear rate
GPC	gel permeation chromatography
HPLC	high-pressure liquid chromatography
I(θ)	normalized intensity of scattering
K	Mark-Houwink parameter in dl/g
k'	Huggins parameter
LS	light scattering
Mn,Mv,Mw	number, viscosity and weight, average molecular weight, respectively
MW	molecular weight
NC	nitrocellulose
n_o,n_{ref}	refractive index of solvent and benzene, respectively
N_A	Avogadro's number
PS	polystyrene
R	gas constant
R_{ref}	Rayleigh ratio of benzene
r	radius of the viscosimeter capillary tube
$\overline{S_z^2}$	Z average mean square radius of gyration

T	absolute temperature
THF	tetrahydrofuran
t	flow time in sec in the viscosimeter
u	the variable $\frac{16\pi^2 n_s^2 \sin^2\theta/2}{3\lambda_o^2}$
UV	ultraviolet
V	total volume discharged through the viscosimeter capillary tube in t sec
V_e	elution volume in GPC
α	represents $\frac{\sin\theta}{1 + (\frac{1-\rho}{1+\rho})\cos^2\theta}$
Δ, Δ°, Δ_{ref}	output readings of the LS photometer for the solution, solvent and benzene, respectively
$[\eta]$, η_r, η_{sp}	intrinsic, relative and specific viscosity, respectively
θ	observation angle in the LS photometer
λ_o	wavelength of incident light in vacuum
π	osmotic pressure
ρ	depolarization factor

1.0 INTRODUCTION

Nitrocellulose (NC) is one of the main ingredients used in gun and rocket propellants. It is well known that some properties of NC (Ref. 1) affect the processability and ballistic performance of the propellant derived from it. The object of this work is to determine if there is any difference in the solution properties of NC samples obtained from various cellulose sources and nitration processes and of different nitrogen content. For this purpose, one cotton and four wood NC samples were characterized at 25°C in different solvents using viscometry, membrane osmometry, light scattering (LS) and gel permeation chromatography (GPC) techniques.

This work was performed at DREV between January 1979 and June 1981 under PCN 21C07, Gun Propellants.

2.0 EXPERIMENTAL

2.1 Samples

The characterized samples are listed in Table I. The first three samples were obtained from Mr. J.E. Stutchbury, Australian National Leader (TTCP Technical Panel W-4). Sample 1 was produced by the Explosives Factory at Maribyrnong from Maryvale pine pulp wood paper. Sample 2 was an experimental lot produced at Mulwala Explosives Factory from Australia Shoalhaven papered cotton linters. Sample 3 was a pyro wood NC made from Rayonier Q alpha cellulose board. Samples 4 and 5 were obtained from Mr. R. Heddle, Marketing Manager at EXPRO Chemical Products in Valleyfield, Quebec, Canada.

TABLE I

Nitrocellulose samples

Sample	Country of Origin	Cellulose Source	% N	Remarks
1	Australia	Wood	12.2	Displacement nitrated (1968) pine pulp
2		Cotton	12.74	Mechanically nitrated (1974) papered cotton linters
3		Wood	12.6	Mechanically nitrated (1974) α cellulose board
4	Canada	Wood	12.6	Pyro (lot A-1-42)
5		Wood	13.42	High grade (lot charge 2692)

2.2 Viscosity

Viscosity measurements were made at 25°C in THF, ethyl acetate and acetone. Three Ubbelohde viscosimeters calibrated with mercury were used in this study. The average rate of shear $G = \frac{8V}{3\pi r^3 t}$ was in the range from 250 to 3000 s^{-1}. The data were extrapolated first to zero rate of shear and then to zero concentration in the manner described in Ref. 2.

Low concentrations were used (below 0.5 g/dl). Both $[\eta]$ and k' were obtained from the Huggins relation:

$$\frac{\eta sp}{c} = [\eta] + k'[\eta]^2 c$$

In some experiments, the solutions were centrifuged for two hours at 30,000 g.

2.3 Osmotic Pressure

Osmotic pressure measurements were made at 25°C with a Hewlett-Packard model 501 high-speed membrane osmometer and using Schleicher and Schuell type membranes of regenerated cellulose with a pore size of 5 nm. Ethyl acetate and THF were used as solvents; the solution concentrations were between 0.10 and 1.0% w/v. Prior to the measurement the solutions were filtered through Versapor membranes (porosity 0.9 μm) made by the Gelman Instrument Company. $(\pi/c)^{\frac{1}{2}}$ was plotted against c. Mn and A_2 were determined from the intercept and the slope respectively according to the following relations:

$$Mn = \frac{RT}{(\text{intercept})^2}$$

$$A_2 = \frac{2}{Mn} \frac{(\text{slope})}{(\text{intercept})} \times 1000 \qquad \text{ml mole/g}^2$$

2.4 Light Scattering

Light scattering measurements were carried out on an SOFICA photometer (model 42000) using unpolarized light at two different wavelengths, 436 and 546 nm. The samples were characterized at 25°C in ethyl acetate and THF. Solutions were centrifuged for two hours at 30,000 g and the top 40% of each volume was removed with a syringe and then filtered and transferred to the LS cell. Versapor membranes (porosity 0.9 μm) made by the Gelman Instrument Company were used for the filtration.

The LS photometer was calibrated with benzene and values of 16.3×10^{-6} cm^{-1} and 48.5×10^{-6} cm^{-1} were chosen (Ref. 3) for the Rayleigh ratio of this liquid at 546 and 436 nm respectively. In each solvent, scattered intensities were recorded for five different concentrations between 0.08 and 0.4% and at various observation angles ranging from 30° to 150°. The solution concentrations were determined

by evaporation. The (dn/dc) measurements were carried out at 436 and 546 nm using a differential refractometer (model BP-2000 V) made by the Phoenix Precision Instrument Company.

2.5 GPC

The chromatograph used was a Waters Associates (model 244A) instrument operating at room temperature using THF as a solvent with a flow rate of 1.0 ml/min. The THF was HPLC grade, without stabilizer, supplied by Caledon Laboratories.

Five microstyragel columns were used with medium porosities of 10^6, 10^5, 10^4, 10^3 and 100 Å. A Waters UV Absorbance Detector (model 440) was used at 254 nm. Data were analyzed by a Waters Data Module (model 730).

To prevent column plugging, a Waters in-line precolumn filter (2 micron porosity) was installed between the injector and the first column. All the solutions were filtered through Versapor membranes prior to injection.

3.0 RESULTS AND DISCUSSION

3.1 Viscosity

The $[\eta]$ values for the NC samples in acetone, ethyl acetate and THF are listed in Table II. The centrifugation had a slight effect on the results as can be seen in the case of THF where the $[\eta]$ values for centrifuged solutions are approximately 12-20% lower. For samples 1, 3 and 4, the variation of the $[\eta]$ value as a function of the solvent is less than 10% and within experimental error. However for samples 2 and 5, the $[\eta]$ value increases slightly as the polarity of the solvent

decreases. For samples 2 and 5 the [η] value in THF is about 30% higher than in acetone. This would indicate that samples 2 and 5 are less soluble in polar solvents.

The Huggins parameter (k') values of the NC samples in different solvents are reported in Table III. k' is practically constant in THF for all the samples. In ethyl acetate, k' is 35% higher for samples 2 and 5 compared to the other samples. As the polarity of the solvent increases, the difference in k' becomes still more apparent, as observed in acetone, where k' is twice that for samples 2 and 5 compared to samples 1, 3 and 4. As k' is relatively higher in bad solvents, sample 2 (cotton NC) and sample 5 (wood NC with high nitrogen content) are thus less soluble in polar solvents. This correlates with the conclusion derived from the intrinsic viscosity results.

TABLE II

[η] values in dl/g ±10%

Sample	Acetone	Ethyl Acetate	THF
1	3.20	3.85	3.40 (2.88)
2	3.00	3.65	4.00 (3.34)
3	3.50	4.08	3.60 (3.22)
4	4.50	4.94	4.07 (3.60)
5	3.40	4.00	4.30

( ) centrifuged

TABLE III

Huggins parameter (k')

Sample	Acetone	Ethyl Acetate	THF
2,5	0.50 ± 0.04	0.61 ± 0.06	0.53 ± 0.06
1,3,4	0.23 ± 0.03	0.46 ± 0.07	0.46 ± 0.07

TABLE IV

Osmometry results

Sample	M_n 10^{-4} ± 10%		A_2 10^4 ± 10% (ml mole/g^2)	
	THF	Ethyl Acetate	THF	Ethyl Acetate
1	4.9 (4.9)	3.9	10.2 (11.8)	7.4
2	6.5 (7.2)	5.8	9.2 (12.6)	8.2
3	5.3	4.1	12.9	11.9
4	4.8	4.0	11.7	11.3
5	4.5	4.3	9.7	11.2

( ) not filtered

TABLE V

(dn/dc) values in ml/g ± 5%

λ (nm)	THF		ETHYL ACETATE	
	A	B	A	B
546	0.082	0.075	0.100	0.096
436	0.079	0.071	0.095	0.097

A: not centrifuged

B: centrifuged

3.2 Osmometry

The osmometry results are reported in Table IV. The M_n values in THF are slightly higher than those in ethyl acetate for all the samples. Sample 2 had an M_n of 62,000 ± 5% whereas the other samples had an M_n equal to 46,000 ± 15%.

The filtration of the solutions had a slight effect on the results as can be seen for samples 1 and 2 in THF (not filtered). This was to be expected as M_n is sensitive to the amount of low MW material present in the sample.

The A_2 value for sample 1 is 38% higher in THF than in ethyl acetate, indicating that sample 1 is more soluble in THF. For the other samples, the A_2 values in both solvents are approximately the same and within experimental error.

3.3 Light Scattering

All the NC samples studied had similar (dn/dc) values that did not vary with concentration or wavelength. The centrifugation of the solutions had no significant effect on the (dn/dc) values as shown in Table V. Light scattering data yield three important results: M_w, A_2 and the structure parameter (S_z^2/M_w) according to the relation:

$$\frac{C}{I(\theta)} = \frac{1}{M_w} + \left(\frac{S_z^2}{M_w}\right)u + 2A_2C$$

where

$$I(\theta) = \left(\frac{\Delta - \Delta^\circ}{\Delta\ ref}\right) \frac{\alpha N_a \lambda_\circ^4 R_{ref}}{2\pi^2 n_{ref}^2 (dn/dc)^2 f}$$

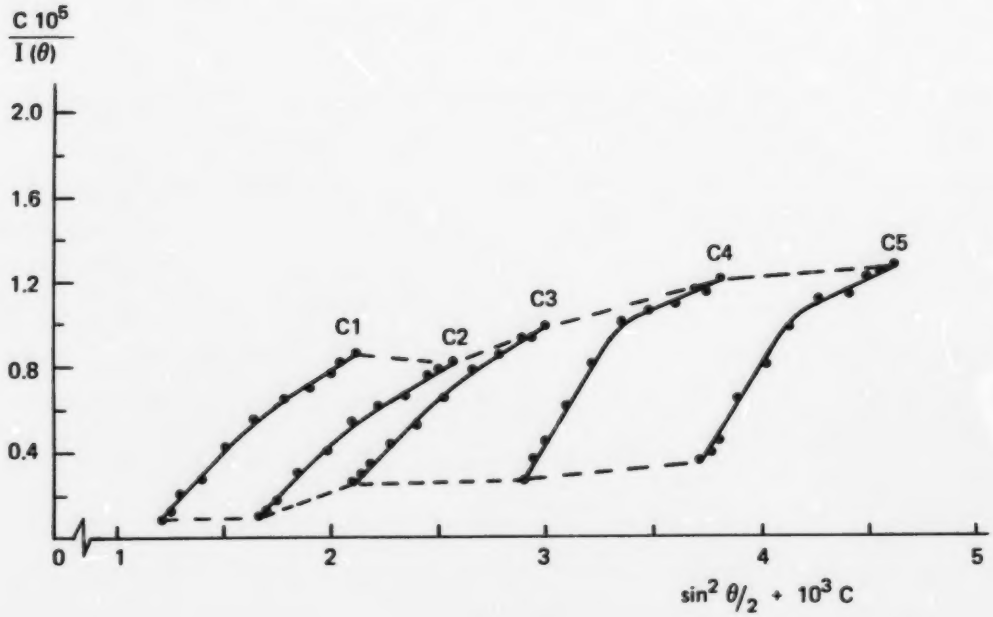

FIGURE 1 - Zimm plot of sample 3 in THF at 436 nm (centrifuged)

TABLE VI

Light scattering results

Sample	$\frac{S_z^2}{M_w}$ (Å^2)	
	THF	Ethyl Acetate
1	1.14 (0.19)	0.53 (0.21)
2	2.09 (1.08)	1.03 (0.82)
3	1.36 (1.07)	0.93 (0.57)
4	1.67 (1.39)	1.31 (1.01)
5	2.08 (1.60)	1.30 (1.28)

( ) not centrifuged

The Zimm plot for sample 3 is drawn in Fig. 1 and exhibits a marked curvature in the angular dependence of scattering and a deviation from linearity in the concentration dependence. These distortions in the Zimm plot are attributed to the microgels (Refs. 4, 5) present in the solutions. For these reasons, M_w and A_2 could not be determined accurately from the Zimm plot.

Nitrocellulose in solution consists of a molecularly dispersed portion and a microgel portion that can be reduced by centrifugation and by decreasing the solution concentration. As the concentration is lowered, the slope at high angles increases gradually until it reaches a maximum and constant value. The slope at high angles and low concentrations yielded the values of (S_z^2/M_w) of the NC molecularly dispersed component that are reported in Table VI.

The (S_z^2/M_w) values between brackets were obtained for solutions that were not centrifuged and the clarification was accomplished only by filtration. The centrifugation of the solutions for sample 1 increased the ratio (S_z^2/M_w) by a factor of 6 in THF and 2.5 in ethyl acetate due to the high microgel content compared with the other NC samples where this ratio was either constant or increased by centrifugation from 20% to 90% depending on the sample and the solvent. The microgel effect decreases the slope at high angles, as has already been illustrated in the Zimm plot. Consequently, the centrifugation effect on the (S_z^2/M_w) values is much more important for samples with a high microgel content as observed for sample 1. For centrifuged solutions, the ratio (S_z^2/M_w) in ethyl acetate is generally lower than in THF, especially in the case of samples 1 and 2 where the (S_z^2/M_w) value in ethyl acetate is nearly half that in THF. Samples 1 and 2 thus appear more soluble in THF than in ethyl acetate, which is in agreement with the viscosity results (for sample 2) and with the osmometry results (for sample 1).

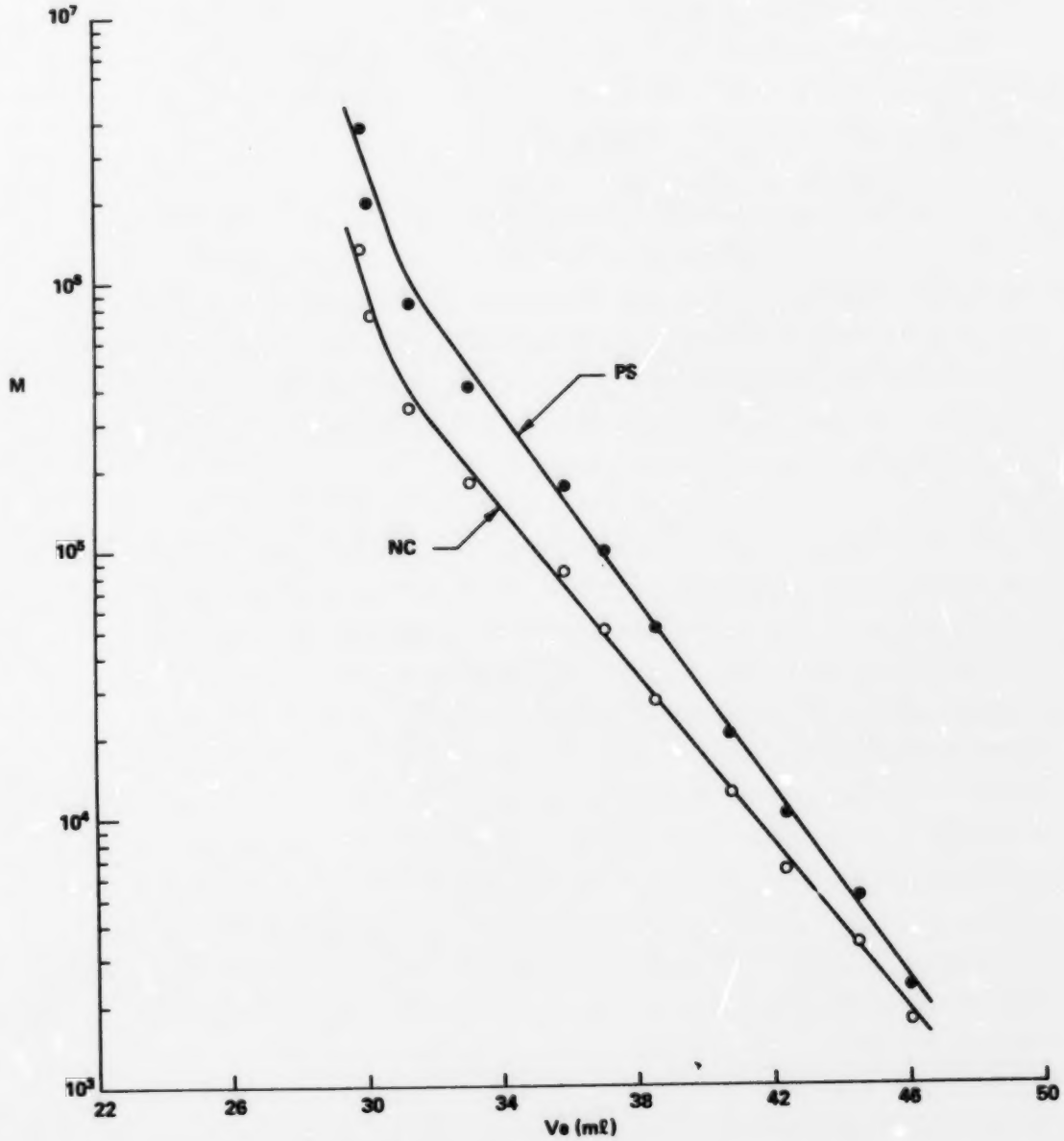

FIGURE 2 - GPC calibration curves

3.4 GPC

3.4.1 Calibration

Calibration of the instrument was performed with polystyrene (PS) standards by plotting log M vs Ve as shown in Fig. 2. The conversion from PS to NC molecular weights was done by combining the hydrodynamic volume $[\eta]M$ relationship proposed by Benoit (Ref. 6) with the Mark-Houwink equation $[\eta] = KM^a$. For a given elution volume, both PS and NC have the same hydrodynamic volume $[\eta]M$ and the following relation is obtained:

$$\log M_{NC} = \left(\frac{1}{1 + a_{NC}}\right) \log \frac{K_{PS}}{K_{NC}} + \left(\frac{1 + a_{PS}}{1 + a_{NC}}\right) \log M_{PS} \qquad [1]$$

There is much dispersion in the Mark-Houwink parameters 'a' and K listed in the literature (Refs. 7, 8, 9, 10) for NC and PS. However the dispersion is much greater in the case of NC: the exponent 'a' varies from 0.76 to 1.14 whereas the K parameter value varies between 8.3×10^{-4} and 0.07×10^{-4} (dl/g) respectively. For PS the exponent 'a' varies from 0.72 to 0.65 whereas the K value varies between 1.1×10^{-4} and 2.9×10^{-4} $\left(\frac{dl}{g}\right)$ respectively.

For a polydisperse system, the Mark-Houwink relation is:

$$[\eta] = KM_w^a \left(\frac{Mv}{Mw}\right)^a = KM_n^a \left(\frac{Mv}{Mn}\right)^a \qquad [2]$$

For a Schulz-Flory MW distribution (Ref. 7), the polydispersity factors $\left(\frac{Mv}{Mw}\right)^a$ and $\left(\frac{Mv}{Mn}\right)^a$ are listed in the Polymer Handbook (Ref. 7) for different values of the parameter 'a'.

By combining the viscosity and osmometry results in THF and using eq. 2, a value of 0.56×10^{-4} (dl/g) was obtained for the K parameter for NC for an exponent 'a' of 0.9. The 'a' and K parameters for PS were determined from the Mark-Houwink relation, and by choosing the $[\eta]$ & M values of PS standards that were used to draw the universal calibration curve ($\log[\eta]M$ vs Ve), which was reported in another article (Ref. 11). The parameters 'a' and K obtained in this manner for PS were equal to 0.71 and 1.34×10^{-4} (dl/g) respectively. Then by combining these 'a' & K parameters for PS with those found for NC and using eq. 1, the following relation was obtained:

$$M_{NC} = 1.58\ M_{PS}^{0.90}$$

Therefore, by using this relation, the PS calibration could easily be transposed to draw the NC calibration curve shown in Fig. 2.

MW averages of the NC samples reported in Table VII were obtained from this NC calibration curve. All MW averages were extrapolated to zero concentration as explained in Subsection 3.4.2. All the NC samples had approximately the same value for M_w (2.4×10^5 ± 12%). Sample 2 had an Mn value (58,000) relatively higher than the other samples (42,000) which is in agreement with the osmometry results. The polydispersity of samples 4 and 5 ($M_w/M_N = 6.4$) was relatively higher than the other samples ($M_w/M_N = 4.7 \pm 8\%$).

TABLE VII

GPC results in THF

Sample	$M_w 10^{-5}$	$M_n 10^{-4}$	$\frac{M_w}{M_n}$
1	2.1	4.4	4.8
2	2.5	5.8	4.3
3	2.2	4.3	5.1
4	2.7	4.3	6.3
5	2.7	4.1	6.6

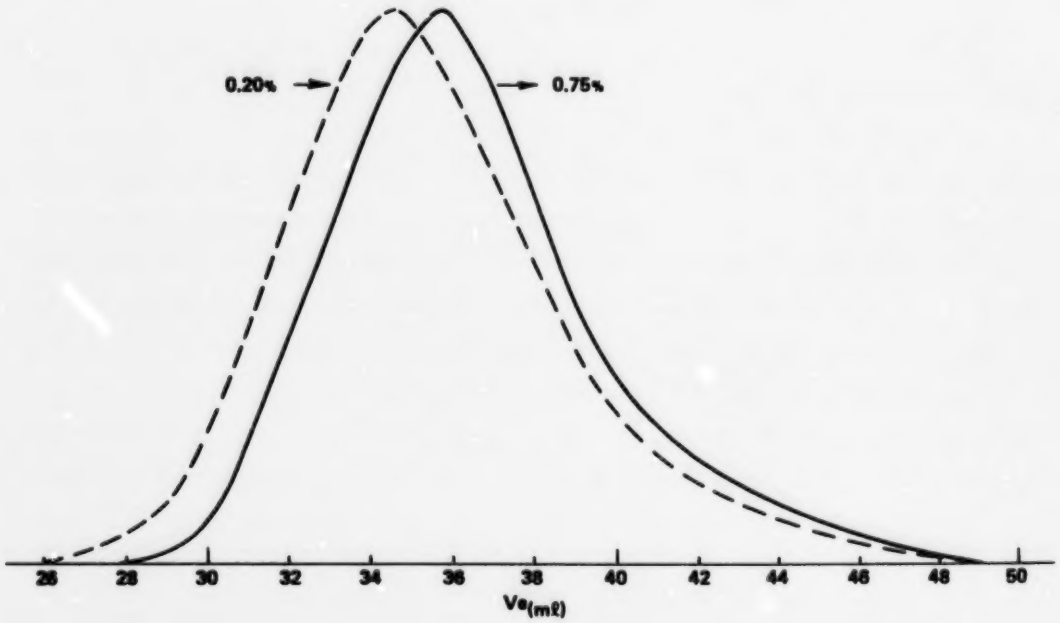

FIGURE 3 - Concentration effect for sample 1

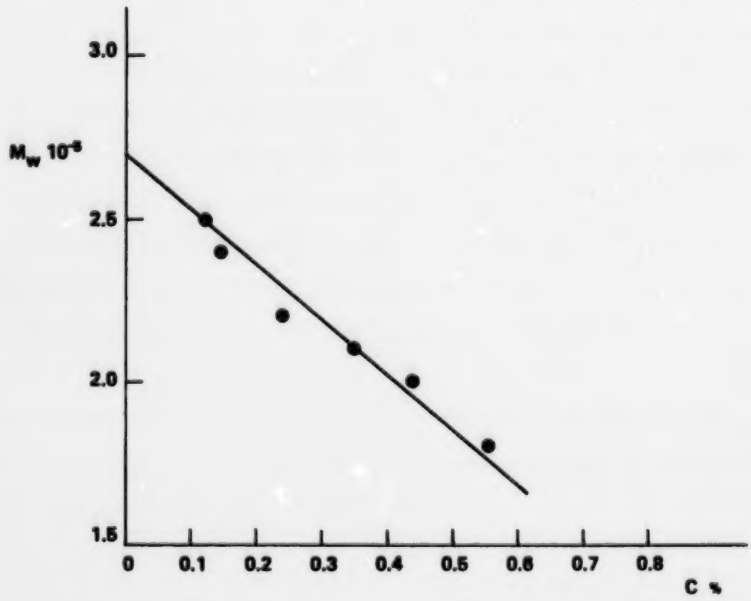

FIGURE 4 - Concentration effect for sample 4

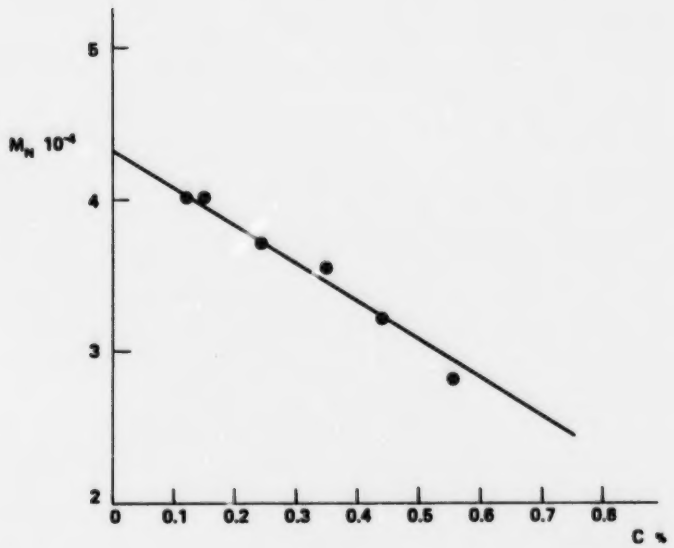

FIGURE 5 - Concentration effect for sample 4

3.4.2 Concentration Effect

Figure 3 shows the concentration effect on the NC chromatogram: as the concentration is increased, the peak shifts towards the lower MW. This effect could be explained by 'viscous fingering': as the solution enters the first column, it creates a high viscosity zone that increases the elution volume and causes chromatogram distortion and tailing. As the viscosity increases with concentration as well with MW, this effect will be more pronounced for higher molecular weights.

This concentration effect, which was also reported in Ref. 12 is not unique to NC but was also observed for other polymers such as ethyl cellulose (Ref. 13). For this reason MW averages are extrapolated to zero concentration. Figures 4 and 5 show the concentration effect on M_W and M_N respectively.

4.0 CONCLUSIONS

In most of the methods investigated, and especially for LS, the results varied according to the technique used to clarify the solutions, hence the necessity to compare results obtained for ones treated in the same manner. The solution properties of NC are affected by the presence of a gel-like material even when the larger microgels have been removed by centrifugation. These microgels could well be branched, cross-linked or partially nitrated polymers. The microgels increase the MW of the polymer considerably, but their contribution to its intrinsic viscosity is slight. Therefore the presence of microgels distorts the Mark-Houwink relationship between M and $[\eta]$. This could explain the great dispersion in the Mark-Houwink parameters for NC reported in the literature.

Gel permeation chromatography is a valuable tool for the rapid determination of the various MW averages as well as the MW distribution of NC once a valid calibration curve is established. Unfortunately the GPC technique cannot detect small structural and morphological differences which may exist between different NC samples. On the other hand, techniques such as viscometry, osmometry and LS clearly showed the existence of some differences in the solution properties among the investigated NC samples:

a) sample 1 had a high microgel content, and
b) samples 1, 2 and 5 are less soluble in polar solvents.

These differences in solution properties arise probably from differences in morphology and microstructure between the NC samples in terms of:

a) degree of crystallinity of the fibres;
b) degree of substitution and nitrogen content distribution; and
c) distribution of nitrate ester groups both around a single glucose unit and along the cellulose chains.

In this study, NC samples from various cellulose sources and nitration processes and of different nitrogen content were characterized in solution. From the results obtained, we cannot conclude whether the structural and morphological differences among the NC samples resulted from the method of preparation or from the cellulose origin (wood or cotton).

Sample 1 (wood NC), produced by the displacement method and with a relatively lower nitrogen content, had a much higher microgel content than the other NC samples. The origin of microgels in the NC would then be more related to the nitration process than to the cellulose source (wood or cotton).

To study morphology and microstructure differences between NC samples in detail, other techniques should be investigated, such as nuclear magnetic resonance, X-ray spectroscopy and differential scanning calorimetry.

5.0 ACKNOWLEDGEMENTS

The author would like to express his sincere thanks to Mr. A. Nolet for his valuable technical assistance.

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Un échantillon de nitrocellulose (NC) de coton et quatre échantillons de NC de bois ont été caractérisés à 25°C par viscosimétrie, osmométrie à membrane, chromatographie par perméation de gel ("GPC") et diffusion de la lumière (DL). Dans la plupart des méthodes examinées, les résultats variaient selon la technique utilisée pour clarifier les solutions. Le paramètre de Huggins calculé à partir des mesures de viscosité était pratiquement constant dans le tétrahydrofurane (THF), mais était plus élevé dans l'acétone et l'acétate d'éthyle dans le cas du NC de coton et du NC de bois "high grade" (13.4% N). Les mesures de GPC ont été effectuées dans le THF; un effet de concentration a été observé et les masses moléculaires moyennes ont été extrapolées à concentration nulle. La polydispersité des échantillons était relativement élevée. Les mesures de DL ont été effectuées dans le THF et l'acétate d'éthyle à 546 et 436 nm. Le NC en solution se compose d'une portion moléculaire dispersée et d'une portion de microgel qui peut être réduite par centrifugation et en diminuant la concentration de la solution. La présence de microgels dans les solutions produisait des distorsions dans les diagrammes de Zimm, i.e. une courbure prononcée dans la variation angulaire de la diffusion et une déviation de la linéarité pour la variation de la diffusion avec la concentration. La pente aux angles élevés a fourni le rapport entre la moyenne "Z" du carré moyen du rayon de giration et la moyenne pondérale de la masse moléculaire.

CRDV R-4296/83 (NON CLASSIFIE)

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DREV R-4296/83 (UNCLASSIFIED)

Research and Development Branch, DND, Canada.
DREV, P.O. Box 8800, Courcelette, Que. G0A 1R0

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One cotton nitrocellulose (NC) and four wood NC samples were characterized at 25°C by viscometry, membrane osmometry, gel permeation chromatography (GPC) and light scattering (LS). In most of the methods investigated, the results varied according to the technique used to clarify the solutions. The Huggins parameter computed from the viscosity measurements was practically constant in tetrahydrofuran (THF) but was higher in acetone and ethyl acetate in the case of cotton and high-grade wood NC (13.4% N). GPC measurements were carried out in THF; a concentration effect was observed and molecular weight averages were extrapolated to zero concentration. The polydispersity of the samples was relatively high. LS measurements were carried out in THF and ethyl acetate at 546 and 436 nm. NC in solution consists of a molecularly dispersed portion and a microgel portion that can be reduced by centrifugation and by lowering the solution concentration. The presence of microgels in the solutions produced distortions in Zimm plots, i.e. a marked curvature in the angular dependence of scattering and a deviation from linearity in the concentration dependence. The slope at high angles yielded the ratio of the Z average mean square radius of gyration to the weight average molecular weight.

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